

METHOD OF CLEANING SEMICONDUCTOR SUBSTRATE CONDUCTIVE LAYER  
SURFACE

Field of the Invention

5 [0001]

The present invention relates to a method for cleaning a surface of a conductive layer on a semiconductor substrate; and, more particularly, to a method for cleaning a surface of a conductive layer exposed through a bottom  
10 portion of a via hole in a dual damascene structure in which a wiring contact hole and a via hole are formed simultaneously.

Background of the Invention

15 [0002]

Conventionally, in a semiconductor device, there has been used a method for depositing and planarizing an interlayer insulating film after a wiring has been formed. As an idea different from this, there is a dual damascene  
20 structure in which a wiring trench and a via hole are formed simultaneously. In this structure, since the via hole can be formed of a same material as that of the wiring trench, an interface resistance of a contact hole can be reduced, and an electro-migration tolerance can be enhanced.  
25 Especially, in the dual damascene structure, hitherto demands for enhancing a film coatability to prevent a void

from being formed between wirings become unnecessary, because the interlayer insulating film is always deposited on a planar surface.

Reference 1: Japanese Patent Laid-open Application No.  
5 2002-26121 (Paragraph 0031, Fig. 6)  
[0003]

A fabrication process of this dual damascene structure includes a process for cleaning the surface of the conductive layer exposed through the bottom portion of the  
10 via hole. In many cases, etching residue of organic materials such as photoresist or the like lies on the surface of the conductive layer beneath the bottom portion of the via hole. Further, a native oxide film is inevitably formed on the surface of the conductive layer. For example,  
15 in case the conductive layer is copper, copper oxide (CuO) is formed. Such residual organic material or oxide causes a problem in that it causes an electric resistance of a via hole portion to increase.

[0004]  
20 Reference 1 discloses that the increase in the electric resistance of the via hole portion can be prevented by plasma processing a surface of a low-k film to form a detailed surface modification layer.

[0005]  
25 Further, as a conventional method other than that disclosed in Reference 1, there is a method for cleaning the

surface of the conductive layer exposed through the bottom portion of the via hole. In this method, although the residual organic material is decomposed to be removed by injecting argon ions, since injecting the argon ions does not involve an ashing, residual organic material cannot be removed completely. Hence, the surface cannot be cleaned sufficiently. Further, native oxide cannot be removed. In addition, a damage is inflicted on an insulating film on a side wall of the via hole when the argon ions are injected, thus causing an adverse effect on the dielectric constant (k value).

#### Summary of the Invention

[0006]

It is, therefore, an object of the present invention to provide a method for cleaning a surface of a semiconductor substrate capable of sufficiently removing residual organic material and/or natural oxide, thereby preventing a damage on a side wall insulting film of a via hole, and preventing an adverse effect on the dielectric constant (k value).

[0007]

In accordance with a first aspect of the present invention, there is provided a method for cleaning a surface of a conductive layer on a semiconductor substrate placed in a reaction chamber, wherein plasma containing hydrogen is

generated in the reaction chamber, and the surface of the conductive layer is cleaned by being reduced therewith.

[0008]

5 Since the oxide film can be removed by cleaning a surface of a conductive layer by generating plasma containing hydrogen in the reaction chamber such that the surface of the conductive layer is cleaned by being reduced therewith, the cleaning can be performed without increasing the electric resistance and the dielectric constant (k value).

10 [0009]

Further, the residual organic material on the surface of the conductive layer is removed by being ashed with the plasma.

15 [0010]

Further, an insulating layer is formed on the surface of the conductive layer, a via hole for exposing a part of the conductive layer is formed in the insulating layer, and the surface of the conductive layer exposed through a bottom portion of the via hole is cleaned by the plasma.

20 [0011]

Further, an upper insulating film is further deposited on the insulating layer, and a wiring trench for exposing the via hole is formed in the upper insulating film, the exposed surface of the conductive layer being cleaned by the plasma after the upper insulating film has been formed.

25

[0012]

Further, the above-mentioned steps of cleaning is performed using a high density plasma processing at a low electron temperature.

5 [0013]

Further, the high density plasma processing is performed by forming a uniform electric field in the reaction chamber, the high density plasma being generated using microwave.

10 [0014]

Further, the high density plasma processing is performed under an atmosphere of gaseous mixture containing hydrogen and helium, and ratio of the helium with respect to the hydrogen is set to be 0.005 to 20.

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#### Brief Description of the Drawings

[0015]

Fig. 1 shows a cross sectional view of a plasma processing apparatus used for cleaning a dual damascene structure;

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Fig. 2 illustrates a partial cutaway perspective view of a slot plate installed in the plasma processing apparatus shown in Fig. 1;

Fig. 3 offers a cross sectional view showing a dual damascene structure on a semiconductor substrate;

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Fig. 4 describes ashing rates of respective processing

Fig. 4 describes ashing rates of respective processing gases;

Fig. 5A represents k values of the insulating film for carrying out the processes using respective processing gases;

Fig. 5B shows  $\Delta k$  values of the insulating film for carrying out the processes using the respective processing gases;

Fig. 6 presents etching rates of respective processing gases with respect to SiOCH;

Fig. 7 depicts flow rate ratios of He/H<sub>2</sub> gas;

Fig. 8 describes flow rate ratios of N<sub>2</sub>/H<sub>2</sub> gas;

Fig. 9 sets forth oxygen reduction characteristics depending on emitting time when plasma using the He/H<sub>2</sub> gas is emitted onto CuO; and

Fig. 10 is a flow chart showing an operation sequence in accordance with the cleaning method of the present invention.

## Detailed Description of the Preferred Embodiment

[0016]

Hereinafter, a preferred embodiment in accordance with the present invention will be described with reference to accompanying drawings.

[0017]

Fig. 1 shows a cross sectional view of a high density

plasma processing apparatus 10 used for cleaning a dual damascene structure. Fig. 2 illustrates a partial cutaway perspective view of a slot plate installed in the high density plasma processing apparatus shown in Fig. 1.

5 [0018]

The high density plasma processing apparatus 10 includes a processing chamber 11 having a substrate support 12 for supporting a semiconductor wafer W of a dual damascene structure. Gas in the processing chamber 11 is exhausted from an exhaust pipe 135 to a gas exhaust system 124 via a gas exhaust opening 136, an exhaust chamber 137 and an exhaust pipe opening 134. Further, the substrate support 12 includes a heater 121 for heating the semiconductor wafer W. The heater 121 is driven by an external heater power supply 122.

15 [0019]

At an upper portion of the processing chamber 11 is formed an opening opposite to the semiconductor wafer W on the substrate support 12. The opening is closed up tightly by a dielectric plate 13 made of quartz, aluminum oxide or aluminum nitride. On an upper portion (outer portion) of the dielectric plate 13 is arranged a slot plate 14 functioning as an antenna (planar antenna) as shown in Fig. 2.

25 [0020]

The slot plate 14 includes a circular conductive plate

141 made of a circular thin copper plate coated with metal or silver, and a plurality of T-shaped slits 142 are formed on the circular conductive plate 141. Further, the slots are formed radially in a direction of a radius, and gaps between the slits are preferably set to be  $\lambda_g/2$  or  $\lambda_g$ . An electric field distribution that is uniform in the processing chamber 11 is formed by the slits 142.

[0021]

On an upper portion (outer portion) of the slot plate 14 is arranged a dielectric plate 15 made of quartz, alumina and aluminum nitride. The dielectric plate 15 is also referred to as a retardation wave plate or a wave slow plate, and shortens a wavelength of a microwave by reducing a propagation velocity thereof, improving a propagation efficiency of the microwave radiating from the slot plate 14. On an upper portion (outer portion) of the dielectric plate 15 is disposed a covering member 16 made of metal (aluminum, stainless steel, or the like) to cover the slot plate 14 and the dielectric plate 15.

[0022]

In the covering member 16 is installed a coolant channel 16a through which coolant flows, suppressing, for example, damages on members by refrigerating the dielectric plate 13 and the slot plate 14. Further, at a central portion of an upper end of the processing chamber is installed a rectangular waveguide 132 or a coaxial waveguide



132 for introducing a microwave from the microwave  
generating source 128. At walls of the processing chamber  
11 are installed gas nozzles 22 for introducing gas,  
allowing various gases to be introduced as shown in Fig. 1.

5 [0023]

By opening a gate valve 125, the semiconductor wafer W  
can be transferred via a transfer port 133.

[0024]

On outer parts of the walls of the processing chamber  
10 11 is formed the coolant channel 24 in a manner that it  
surrounds the chamber. A gas supply source 130, a gas  
exhaust system 124, a heater power supply 122 and the like  
are controlled by a controller 124, the controller including  
a CPU, memory storage media like a ROM and RAM, a hard disk,  
15 a CD-ROM driver and a transfer unit (not shown). By storing  
a software for performing the method for cleaning a surface  
of a conductive layer on the semiconductor substrate in  
accordance with the present invention in the hard disk or  
the ROM, or externally supplying the above-mentioned  
20 software by the CD-ROM or the like to transfer it to the RAM,  
the CPU in the controller 124 carries out the cleaning  
method in accordance with the present invention.

[0025]

Fig. 3 offers a cross sectional view showing a dual  
25 damascene structure. As shown therein, interlayer  
insulating films 2 and 3 made of low-k films such as SiCOH

are formed on a conductive layer 1 which is a Cu wiring layer. A via hole 4 functioning as a contact portion is formed in the interlayer insulating film 2, and a part of the conductive layer 1 is exposed through a bottom portion of the via hole. In the interlayer insulating film 3 is formed a wiring trench 5 for exposing the via hole 4. The via hole 4 and the wiring trench 5 are formed by etching. However, at that time, residual organic material 6 such as photoresist and the like remains on a surface of the conductive layer 1, and a copper oxide film 7 is formed thereon.

[0026]

In accordance with the present invention, after a substrate of the dual damascene structure has been transferred into the processing chamber 11 in the high density plasma processing apparatus 10 shown in Figs. 1 and 2, a gas including hydrogen is introduced into the processing chamber 11, and hydrogen-containing plasma is generated in the processing chamber 11. Then, the residual organic material 6 on side walls of the interlayer insulating films 2 and 3 is decomposed and removed by an ashing, and, at the same time, the copper oxide film 7 on the surface of the conductive layer 1 exposed through the via hole 4 is reduced to copper (Cu) by controlling a pressure in a reaction chamber and a duration of the hydrogen-containing plasma generation.

[0027]

It can be considered to use processing gases such as an Ar/O<sub>2</sub>/He gas, an Ar/N<sub>2</sub>/H<sub>2</sub> gas and an Ar/He/H<sub>2</sub> gas for removing the residual organic material 6 by generating plasma using the high density plasma processing apparatus 10. However, more preferably, by performing a plasma processing with a high density plasma of 10<sup>11</sup> to 10<sup>13</sup>/cm<sup>2</sup> at a low electron temperature (0.7 eV to 2 eV) by the high density plasma processing apparatus 10 under an atmosphere of the Ar/He/H<sub>2</sub> gas to ash the residual organic material 6, the residual organic material 6 can be decomposed to be removed, and the copper oxide film 7 can be reduced to copper without inflicting damage on the interlayer insulating films 2 and 3 or increasing the k value.

[0028]

In Fig. 4, ashing rates are compared in cases of ashing the photoresist with the Ar/O<sub>2</sub>/He gas, the Ar/N<sub>2</sub>/H<sub>2</sub> gas and the Ar/He/H<sub>2</sub> gas introduced into the processing chamber 11 under the conditions that the flow rate ratio was 1000/200/200 sccm, the pressure in the processing chamber 11 was 500 mTorr, the output power of the microwave was 1.5 kW, the gap between the dielectric plate 132 and the substrate W was 105 mm, and the temperature in the processing chamber 11 was 250 °C. As shown in Fig. 4, the ashing rate of the Ar/O<sub>2</sub>/He gas including oxygen is the highest, that of the Ar/N<sub>2</sub>/H<sub>2</sub> gas is the second highest, and that of the Ar/He/H<sub>2</sub>

gas is the lowest.

[0029]

Further, Figs. 5A and 5B show  $k$  values and  $\Delta k$  values depending on the processing gas. Specifically, Fig. 5A shows  $k$  values in case of processing the low- $k$  films at a room temperature and at 200 °C by using an Ar gas, the Ar/N<sub>2</sub>/H<sub>2</sub> gas and the Ar/He/H<sub>2</sub> gas, respectively, as the processing gas. Fig. 5B shows differences  $\Delta k$  between the  $k$  values in case of processing the low- $k$  films at a room temperature and at 200 °C. The vertical axes represent the  $k$  value and the  $\Delta k$  value, respectively.

[0030]

As shown in Fig. 5A, in case of using the Ar gas, the difference  $\Delta k$  between the  $k$  values for carrying out the processes at a room temperature and at 200 °C is as small as about 0.15. In case of using the Ar/N<sub>2</sub>/H<sub>2</sub> gas, the difference  $\Delta k$  between the  $k$  values in case of processing at a room temperature and at 200 °C is as large as about 0.35. Further, in case of using the Ar/H<sub>2</sub>/He gas, the difference  $\Delta k$  between the  $k$  values for carrying out the processes at a room temperature and at 200 °C is about 0.12, which means the variation is the smallest in this case. Although the Ar gas has the smallest difference  $\Delta k$  of 0.15, the residual organic material 6 cannot be removed completely as described in the above-mentioned prior art. Therefore, between the above-mentioned two gases including H<sub>2</sub>, the Ar/He/H<sub>2</sub> gas,

having smaller  $\Delta k$ , is more suitable for ashing the residual organic material 6 than the Ar/N<sub>2</sub>/H<sub>2</sub> gas, because the k value does not increase when exposed to the plasma. Further, it is preferable to set the conditions such that a plasma damage is not inflicted on the low k film without raising the k value.

[0031]

Further, Fig. 6 shows etching rates of the respective processing gases with respect to SiOCH(interlayer insulating film). As shown therein, whereas etching rates of the Ar gas, the Ar/N<sub>2</sub>/H<sub>2</sub> gas and the Ar/He/H<sub>2</sub> gas are no more than about 200 Å/min, the etching rates of gases including oxygen such as the Ar/O<sub>2</sub>/He gas, the Ar/O<sub>2</sub>/N<sub>2</sub> gas and the Ar/O<sub>2</sub> gas are as large as about 1900 Å(angstrom)/min. From this, it can be deduced that the etching rates of the Ar gas, the Ar/N<sub>2</sub>/H<sub>2</sub> gas and the Ar/He/H<sub>2</sub> gas are lower than those of the Ar/O<sub>2</sub>/He gas, the Ar/O<sub>2</sub>/N<sub>2</sub> gas and the Ar/O<sub>2</sub> gas, and that the etching rate of the Ar/He/H<sub>2</sub> gas is the lowest, minimizing the damage on the interlayer films 2 and 3.

[0032]

Comparing the results, although the Ar/O<sub>2</sub>/He gas has a high ashing rate and is suitable for removing the residual organic material 6 as described in Fig. 4, it also has a high etching rate, and thus the side walls of the interlayer insulating films 2 and 3 may become etched, increasing the damages on the side walls, making it improper to use the

Ar/O<sub>2</sub>/He gas as the processing gas.

[0033]

On the other hand, although the Ar/He/H<sub>2</sub> gas and the Ar/N<sub>2</sub>/H<sub>2</sub> gas have low ashing rates as shown in Fig. 4, the etching rates thereof are also low as shown in Fig. 6, minimizing the damage on the interlayer films 2 and 3, thus making the Ar/He/H<sub>2</sub> gas and the Ar/N<sub>2</sub>/H<sub>2</sub> gas suitable as the processing gas. Comparing the Ar/He/H<sub>2</sub> gas and the Ar/N<sub>2</sub>/H<sub>2</sub> gas, the Ar/He/H<sub>2</sub> gas is more suitable as the processing gas, because the Ar/He/H<sub>2</sub> gas has a lower  $\Delta k$  than the Ar/N<sub>2</sub>/H<sub>2</sub> gas as shown in Fig. 5.

[0034]

Fig. 7 illustrates flow ratios of the He gas with respect to the H<sub>2</sub> gas in the Ar/He/H<sub>2</sub> gas. As shown therein, the k value is about 2.36 when the flow ratio of the He gas with respect to the H<sub>2</sub> gas is about 0.0 to 0.5. Then, the k value begins to fall when the flow ratio reaches about 0.5. The k value is no more than about 2.35 when the flow ratio of the He gas with respect to the H<sub>2</sub> gas is about 0.7 to 1.75, and therefore, it is preferable to set the flow ratio of the He gas with respect to the H<sub>2</sub> gas to be within this range, as a consequence of only H radicals contributing to the decomposition of the residue material.

[0035]

Fig. 8 illustrates flow ratios of the N<sub>2</sub> gas with respect to the H<sub>2</sub> gas in the Ar/N<sub>2</sub>/H<sub>2</sub> gas. As shown therein,

the k value is about 2.37 to 2.55 when the flow ratio of the N<sub>2</sub> gas with respect to the H<sub>2</sub> gas is about 0.0 to 0.5, and the k value is about 2.55 to 2.6 when the flow ratio is about 0.5 to 1.0, as a consequence of N radicals being  
5 introduced into the insulating films.

[0036]

Comparing the results, it can be seen that the change in the k value with respect to the change in the flow rate ratio is smaller for the Ar/He/H<sub>2</sub> gas than the Ar/N<sub>2</sub>/H<sub>2</sub> gas.  
10 Therefore, by performing the high density plasma processing on the substrate of the dual damascene structure shown in Fig. 3 at a low electron temperature under an atmosphere of the Ar/He/H<sub>2</sub> gas using the high density plasma processing apparatus 10 to ash the residual organic material 6, the  
15 residual organic material 6 can be decomposed and removed most efficiently without inflicting any damage on the interlayer insulating films 2 and 3 and increasing the k value.

[0037]

20 Fig. 9 shows oxygen reduction characteristics when plasma using the He/H<sub>2</sub> gas is emitted onto the copper oxide film 7, wherein the vertical axis represents of the oxygen content (in atomic %).

[0038]

25 As shown in Fig. 9, the copper oxide film originally includes oxygen by 35 atomic %. However, the oxygen content

is reduced to 5 atomic % when CuO is exposed to the He/H<sub>2</sub> plasma for 5 sec, the oxygen content remaining thereat when CuO is exposed to the He/H<sub>2</sub> plasma for 10 sec or 20 sec. Thereafter, the oxygen content is reduced to about 0  
5 atomic % when CuO is exposed to the He/H<sub>2</sub> plasma for 30, 60 or 180 sec, making possible a deduction that the copper oxide film 7 is reduced to Cu to form a clean surface of Cu.  
[0039]

Therefore, it is most preferable to generate hydrogen-  
10 containing plasma using such as Ar/He/H<sub>2</sub> gas to ash the low-k films with the high density plasma at a low electron temperature, so that the residual organic material 6 on the side walls of the oxide insulating film 2 and 3 is removed, and the copper oxide film 7 on the surface of the conductive  
15 layer 1 is reduced to Cu. Preferably, the conditions are as follows: the flow rate ratio of Ar is 500 to 3000 sccm; the flow rate ratio of He is 50 to 1000 sccm; the flow rate ratio of H<sub>2</sub> is 50 to 1000 sccm; the pressure is 100 mmTorr to 5 Torr; the output power is 0.5 to 3 kW; the temperature  
20 is higher than a room temperature; and the processing time below 500 °C is 20 to 600 seconds.

[0040]

Referring the flow chart of Fig. 10, an operation sequence in accordance with the present invention will be  
25 described briefly.

[0041]



After vacuum pumping (S10), a substrate W of the dual damascene structure is transferred from another chamber (not shown) adjacent to the processing chamber 11 via the transfer port 133, and then set in the processing chamber 11 (S12). The gas supply source 130 supplies, typically, the Ar/He/H<sub>2</sub> gas into the processing chamber 11 (S14). Microwaves are propagated from the microwave generating source 128 into the processing chamber 11, thereby generating plasma (S16) (a high density plasma processing with a plasma density of  $10^{11}$  to  $10^{13}$  /cm<sup>2</sup> at a low electron temperature (0.7 to 2 eV). By controlling the duration of the hydrogen-containing plasma generation, the residual organic material 6 on the side walls of the interlayer insulating films 2 and 3 is decomposed and removed by an ashing (S18). At the same time, the copper oxide film 7 on the surface of the conductive layer 1 exposed through a bottom portion of the via hole 4 is reduced to Cu. Thereafter, the plasma is stopped (S20), and then a vacuum pumping is performed (S22). Subsequently, the substrate W is taken out of the processing chamber 11 (S24).

[0042]

Further, while the present invention can clean and remove the residual organic material such as photoresist, the present invention can also be applied to a case of cleaning a surface of a conductive layer of tungsten, copper, WSi, NiSi, CoSi or the like exposed through a wiring contact

hole.

[0043]

5        So far, a preferred embodiment in accordance with the present invention has been described with reference to the drawings. However, the present invention is not limited thereto.

#### Industrial Applicability

[0044]

10        The present invention can be applied to a plasma substrate processing apparatus for reducing the copper oxide film 7 on the surface of the conductive layer 1 to Cu by transferring a semiconductor device into the processing chamber 11; generating hydrogen-containing plasma in the  
15        processing chamber 11; cleaning the conductive layer 1 at a bottom portion of the via hole 4; and decomposing to remove the residual organic material 6 by an ashing.